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THE EFFECT OF HIGH HYDROSTATIC PRESSURE ON THE PERMEABILITY OF --ETC(U)
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(6) THE EFFECT OF HIGH HYDROSTATIC
PRESSURE ON THE PERMEABILITY OF
ELASTOMERS TO WATER

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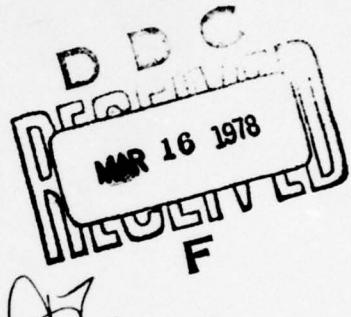
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SUMMARY

The permeability of butyl rubber to pressurized water was measured at 10,000 psi hydrostatic pressure using a relatively simple method which consisted of constructing pouches from rubber, filling these with desiccant and exposing them to pressurized water.

At this high hydrostatic pressure the permeability was found to be smaller than at ambient pressure. This result is significant as it enables one to decide as to the suitability of butyl rubber for construction of hydrophone boots.

Similar results found by other investigators for other polymeric materials were cited.

A thermodynamic analysis of the process of permeation by activated diffusion was made, and the mechanism involved was discussed. It was shown that this seemingly strange behavior could be expected for processes in which permeation occurs by activated diffusion.

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INTRODUCTION

The resistance of polymers and elastomers to penetration by gases, vapors and liquids is an important factor affecting their use. Because of the importance of this property, called permeability, it has been reviewed extensively (1-6) and, for most commercial materials, numerical values have been compiled.

Most of the literature on permeability deals with experiments at ambient and low pressures. The scarcity of data at high hydrostatic pressure is at least partially due to experimental difficulties and because polymeric materials are not as extensively used at high hydrostatic pressures in application where resistance to permeation is important.

The U. S. Naval Applied Science Laboratory became interested in the subject when certain hydrophones immersed at the bottom of the ocean became inoperative due to water leakage and the Laboratory was called upon to assist in the development of a rubber boot to protect such hydrophones in the future. The choice of boot materials was limited to elastomers because the acoustic impedance had to be as close to that of water as possible.

Among the elastomers considered, the least permeable is butyl; consequently a quinoid cured, carbon black filled butyl rubber having an extensive performance history was chosen. A schematic view of a hydrophone, based on a simplified commercial design, is shown in Figure 1. It can be seen from the illustration that the boot is exposed in service, not only to sea water at high hydrostatic pressure but also to castor oil which is used to fill the annular space.

PERMEABILITY MEASUREMENTS

The permeability of this boot material to water vapor at 17.5 mm Hg was measured and found to be sufficiently low to be used with these hydrophones. Because of theoretical considerations, which will be discussed later, it could be predicted that permeability of the boot material to liquid water at high hydrostatic pressure would be essentially the same as at lower pressures. It was decided, however, to verify this point experimentally.

To do this, pouches of the butyl rubber in question were constructed as shown in Figure 2. These were filled either with anhydrous magnesium perchlorate (a desiccant), or lithium chloride, or a mixture of lithium chloride and an aqueous saturated solution of lithium chloride, or a mixture of lithium chloride and castor oil, or a mixture of lithium chloride, saturated lithium chloride and castor oil. These were sealed and immersed in distilled water at 10,000 psi hydrostatic pressure. Control samples were immersed in distilled water at atmospheric pressure. The function of the

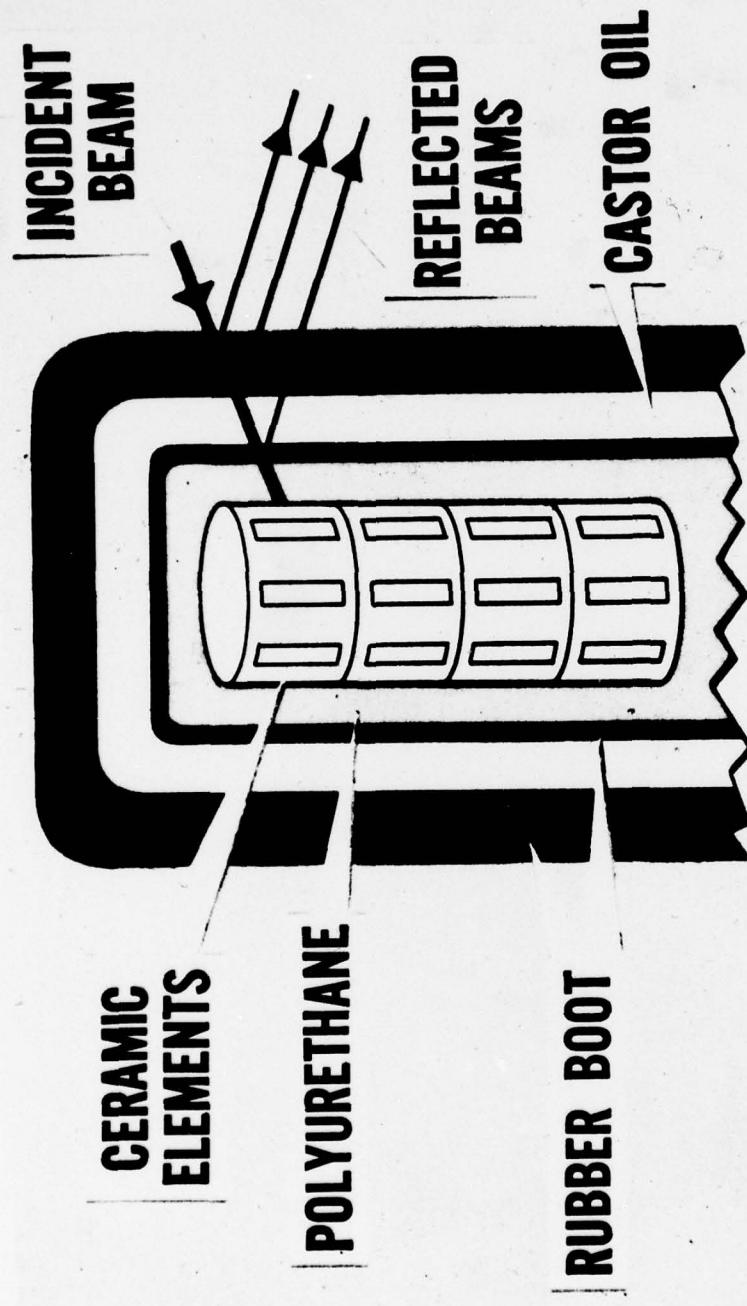
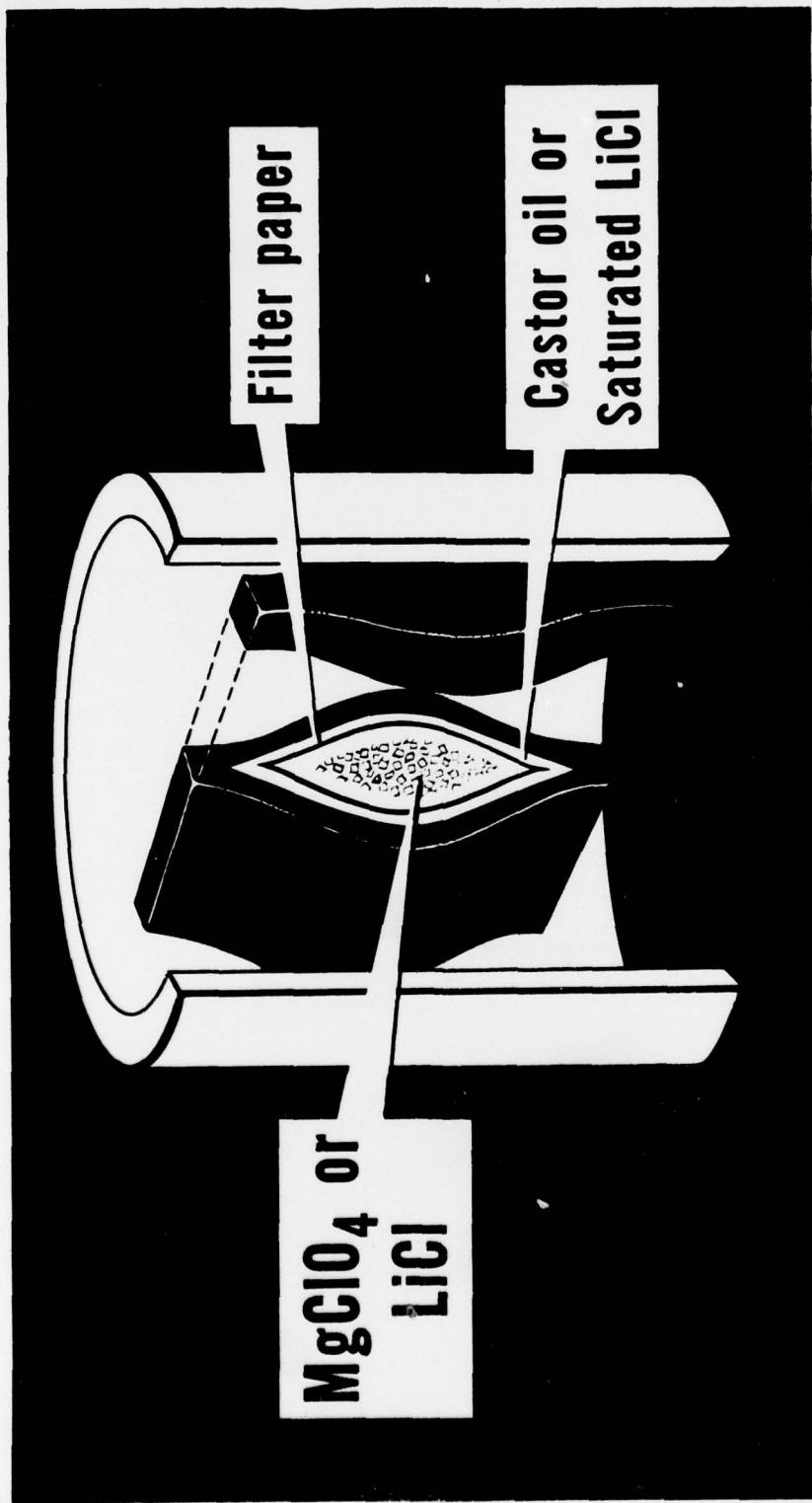


Figure 1
SCHEMATIC DIAGRAM OF BOOTTED HYDROPHONE

BUTYL RUBBER POUCH

Figure 2



liquids was to prevent collapse of the pouches under high hydrostatic pressure which would result in a decreased effective area through which the water could permeate. Saturated lithium chloride was chosen because it has a low water vapor pressure and thus acts as a liquid desiccant. Castor oil was used to determine whether it exerts any deleterious effect on the permeability due to swelling of the rubber, or for any other reason.

After 82 days immersion the pouches were weighed and their increase in weight was determined. The increase that was found includes not only the water that passed through the rubber but also the water that was absorbed and remained in the rubber itself. It is obvious therefore, that the total weight increase exceeds the amount of water that actually passed through the rubber. This weight increase is however, still significant because it sets the upper limit of the permeability constants. These permeability constants were found to be 22×10^{-10} gram water/cm²/cm/hr/mm Hg at ambient pressure and 3.6×10^{-10} gram water/cm²/cm/hr/mm Hg at 10,000 psi hydrostatic pressure.

These data settle the question as to the suitability of the permeability characteristics of this type of rubber for hydrophone boots at high hydrostatic pressures. However, they may be unexpected to the hydrodynamic engineer who is accustomed to dealing with flow through pipes and porous plates in which the flow increases appreciably with increase in hydrostatic pressure.

DATA FROM OTHER SOURCES

Before explaining the reasons why the hydrostatic pressure causes a decrease in permeability of water through butyl rubber, it should be noted that similar results were observed by Herrick (7, 8) and Binning (9). Herrick's method differed from the one described in this paper. He subjected his membranes, supported by a porous plate, to a high hydrostatic pressure on the ingoing side of his apparatus while the outgoing side remained at atmospheric pressure. Some of the data are given in Table 1 below:

TABLE 1

THE EFFECT OF HYDROSTATIC PRESSURE
ON THE PERMEABILITY CONSTANT (a)

Membrane	Permeant	Pressure Range, (psi)	Permeability Constant at:		Remarks
			Low Pressure	High Pressure	
Butyl	Distilled Water	Atm - 10,000	22	3.6	(b)
L.D. Poly- ethylene	Fresh Water	50 - 5,000	47	18	(c)
	Salt Water	50 - 5,000	29	29	(c)
Nylon	Fresh Water	50 - 15,000	295	86	(c)
	Salt Water	50 - 10,000	256	256	(c)
Poly- urethane	Water	0.3 - 3,000	3000	600	(d)
Unidentified Plastic	n-Heptane isooctane mixture	Atm - 150	0.14	0.14	(e)

Notes: (a) Units for all data except the last line: gram water/cm²/cm/hr/mm Hg.

(b) Data obtained at the U. S. Naval Applied Science Laboratory using the method of pouches.

(c) Data from reference (7).

(d) The data at low vapor pressure were obtained at the U. S. Naval Applied Science Laboratory by subjecting the polyurethane sheet to water vapor at 17.5 mm vapor pressure. The data at high hydrostatic pressure are from reference (8) and were obtained by subjecting the polyurethane sheet to pressurized salt water.

(e) Data from reference (9). The permeability units in this case are gal/sq ft/mil/hr.

The above include permeability constants for the permeation of water through polyurethane, polyethylene and nylon and for the permeation of hydrocarbons through an unidentified membrane. In no case did the permeability constant increase with hydrostatic pressure and in half of the cases it decreased appreciably.

DISCUSSION

The lack of increase in permeability with increase in hydrostatic pressure can be understood when it is realized that the permeation of most polymers by gases, vapors, and liquids takes place by a mechanism of activated diffusion which differs from the mechanism of permeation through porous materials.

Permeation by activated diffusion is a three step process. First, the permeating molecule is absorbed at the ingoing surface of the membrane and becomes "dissolved" in it. The rate of solution is governed by the vapor pressure of the permeant at the high pressure side.

In the second step the permeating molecule diffuses within the membrane. Diffusion occurs both in and against the direction of the flow but is greater in the direction of the flow. The most important factors governing the rate of diffusion are the concentration gradient, the activation energy, and the temperature. The concentration gradient is responsible for the fact that more molecules move in the direction of the flow than in the opposite direction, since the probability of a molecule moving is proportional to the concentration at the site from which it is moving. The activation energy is the energy needed to separate the polymer chains and form a new "hole" in which the migrating molecule will be accommodated. The temperature determines the percentage of molecules which will have this energy.

The third and last step is the desorption at the outgoing surface of the membrane. The rate of desorption is governed by the vapor pressure at the outgoing surface. This vapor pressure influences the rate of permeation by determining the concentration gradient within the membrane.

The above mechanism explains why hydrostatic pressure has so little effect on the rate of permeation. The molecules are not caused to move by the force exerted by hydrostatic pressure since this force is too small. What does determine whether a molecule will move at all is the probability of it having sufficient energy to form a new "hole". Whether a molecule that does move will move in the right direction is determined by the concentration gradient which is, in turn, determined by the vapor pressure differential between the ingoing and outgoing sides of the membrane.

The reason why the vapor pressure and not the hydrostatic pressure determines the concentration of the permeant in the membrane can be explained by thermodynamic considerations. The vapor pressure of an ideal vapor equals its fugacity (10) and the vapor pressure of a real vapor is very close to its fugacity. The fugacity, f , is a thermodynamic function defined (11) by equation (1),

$$(1) \quad \mu_i = \mu^* + RT \ln f_i$$

The numerical value of the fugacity, f_i , of a component i is the exponential of the difference between two chemical potentials divided by R , the gas constant, and T , the absolute temperature. The first of these chemical potentials, μ_i , is that of the component i in the state considered. This state may be gaseous, liquid, solid, or a component of a mixture. The second of these chemical potentials, μ^* , is that of a reference state which is a gaseous state of the pure component at a pressure low enough to obey the gas law. If this reference state is chosen so that its pressure is unity, then the fugacity is expressed in the same units.

Another thermodynamic function which is similar to fugacity is the activity, a_i , of the component i , defined (11) by equation (2).

$$(2) \quad \mu_i = \mu^* + RT \ln a_i$$

It is equivalent to fugacity except for the choice of the reference state. If the reference state chosen is the condensed pure state at one atmosphere pressure, then the units of activity are mole fractions (12).

Loosely defined, chemical potential, fugacity, and activity are measures of the ability of the system (the permeant in this case) to perform work and the "desire" of the system to undergo changes. Such a change occurs when the permeant enters and is dissolved in the membrane. If we assume that the rate of absorption and desorption of the permeant by the membrane is fast compared to the rate of diffusion, then the permeant in the surface layers of the membrane is in equilibrium with the permeant in the phase in contact with the membrane. Since two phases in equilibrium have the same chemical potential, therefore ($\mu_i - \mu^*$) which defines the fugacity of the permeant in the phases in contact with the membrane, and ($\mu_i - \mu^*$) which defines the activity of the permeant in the surface layers of the membrane differ only by the constant ($\mu^* - \mu^*$). Consequently their exponentials, the fugacity and activity of the permeant in the corresponding phases are proportional to each other and the proportionality factor is equal to the exponential of ($\mu^* - \mu^*$).

Since the vapor pressure at low and moderate pressures is approximately equal to the fugacity, and since the concentration of a solute in a dilute solution (such as the permeant in a membrane which it does not swell appreciably) is approximately proportional to the activity, therefore, the concentration of the permeant in the surface layers of a membrane is approximately proportional to the vapor pressure in the phases in equilibrium with the membrane.

Vapor pressure is a property which is much easier to comprehend and measure than fugacity. Also, numerical values of vapor pressure and fugacity are practically identical. Therefore, it is justified and customary to use the concept of vapor pressure and not fugacity when discussing factors affecting permeability. This is completely satisfactory as long as vapors and non-pressurized liquids are discussed. However, when discussing the permeability of liquids under high hydrostatic pressure, the use of vapor pressure instead of fugacity necessitates the introduction of the concept of "vapor pressure at high hydrostatic pressure". This is somewhat objectionable since it might be misunderstood to imply that a vapor phase in equilibrium with the pressurized liquid must exist in order for permeation to take place. Such a vapor phase can exist (13, 14), but usually it does not, and is not necessary for permeation. This difficulty will be avoided here by using the term fugacity whenever dealing with pressurized liquids, since the definition of fugacity does not necessitate the existence of a vapor phase. Permeation of vapors and non-pressurized liquids will be discussed in terms of vapor pressure in accordance with common practice.

The amount of permeant, Q , which passes through a membrane is proportional to the exposed area, a , the exposure time, t , the vapor pressure differential, $(p_1 - p_2)$, between the ingoing and outgoing sides of the membrane, and a proportionality constant, called the permeability constant P , and is inversely proportional to the thickness, d .

$$(3) \quad Q = \frac{P a t (p_1 - p_2)}{d}$$

P is a constant only if the permeant does not swell the membrane to a large extent. Situations where this is not the case will be discussed later.

According to equation (3) the permeation rate is proportional to the vapor pressure differential. If the permeant is a vapor then the meaning of vapor pressure is evident. If the permeant is a non-pressurized liquid then the fugacity of the liquid, which is almost exactly equal to the pressure of the vapor in equilibrium with the liquid, is meant. If the permeant is a pressurized liquid then the fugacity is meant again. This fugacity, too, is approximately equal to the vapor pressure if the situation is arranged so that a vapor phase can exist. This can be done either by having the vapor in form of a component of a pressurized gas (13) or by separating the vapor from the liquid by means of a semi-permeable membrane (14) which transmits the permeant but does not transmit the pressure. Both situations are difficult to realize experimentally. It is much easier to calculate this vapor pressure from equation (4).

$$(4) \quad p_{vap} = p_0, vap \exp(p_{hyd} \bar{V}/RT)$$

where p_{vap} is the vapor pressure at the hydrostatic pressure p_{hyd} , p_0, vap is the vapor pressure when the liquid is not pressurized, and \bar{V} is the partial molar volume of the liquid. Equation (4) is the exponential form of equation (6-83) of reference (15). Its derivation, which can be found there, assumes that the vapor obeys the gas law; therefore, its vapor pressure is equal to its fugacity.

Alternatively it is possible to correlate directly the fugacity and activity of a pressurized liquid to the hydrostatic pressure by means of equations (5) and (6), respectively.

$$(5) \quad f = f_0 \exp(p_{hyd} \bar{V}/RT)$$

$$(6) \quad a = a_0 \exp(p_{hyd} \bar{V}/RT)$$

where f_0 and a_0 are the fugacity and activity at ambient pressure. Equation (6) can be derived by integrating equation (31-7) of reference (16) and equation (5) can be derived in a similar manner from equation (26-26) of reference (17) and equation (1) which defines fugacity.

Substitution of numerical values into either equation (4) or (5) shows that at room temperature an increase in hydrostatic pressure of 10,000 psi causes the vapor pressure and the fugacity to increase by about 65%. If the hydrostatic pressure had no influence on the permeability constant then the rate of permeation would also increase by the same amount.

At the higher hydrostatic pressure the permeability constants listed in Table 1 were either considerably smaller or else equal to the corresponding values at the lower pressures. The reasons why the hydrostatic pressure can lower the permeability constant are as follows. The permeability constant comprises various factors which influence the rate of permeation. It is the product of the diffusion constant, D , and the solubility coefficient, S .

$$(7) \quad P = DS$$

and can be further broken down to the Arrhenius type equation (8)

$$(8) \quad P = D_o S_o \exp \left(\frac{-E_D - \Delta H_S}{RT} \right)$$

where D_o and S_o are the pre-exponential factors of the diffusion constant and the solubility coefficient, E_D is the activation energy of the diffusion process and ΔH_S is the heat consumed upon solution.

The solubility coefficient is the ratio of the concentration of the permeant in the outer layers of the membrane and the vapor pressure in the phases in equilibrium with the membrane. As discussed above, this ratio is constant only if the concentration is proportional to the activity. If the hydrostatic pressure is appreciably increased, then the activity of the permeant corresponding to any given concentration increases, though slowly, and the extent of this increase is given by equation (6). This increase in activity causes a decrease in the solubility coefficient since it becomes more difficult to dissolve the permeant in a membrane in which its activity is higher.

An additional point of clarification is necessary to explain why this increased activity does not increase the rate of diffusion. In general, the rate of any chemical or physical process increases if the activity of one of the participants in the process is increased. This is because most changes in activity, being due to changes in concentration, do not increase the energy level of the excited state. Since the increase in activity causes the free energy of the ground state to increase, the difference between the ground state and the excited state decreases, and the rate increases.

In the case of permeation at high hydrostatic pressure the increase in the activity of the ground state is not caused by an increase in concentration but by the necessity of the non-excited molecules to occupy a certain volume at an increased hydrostatic pressure. Since the volume occupied by a non-excited molecule and the volume occupied by an excited molecule can be expected to be the same, therefore the increase in pressure-volume energy needed for occupying this volume will be similar for both, and the increased activity will not increase the rate of diffusion.

The effect which the hydrostatic pressure has on the activity and on the solubility coefficient cannot fully account for the decrease in the permeability constant observed in some of the cases given in Table 1. While, according to equation (6), a pressure of 10,000 psi can be expected to decrease the permeability constant to about 60% of the value observed at ambient pressure, decreases up to one-seventh of this value were observed. The additional decrease could have been caused by the effect of the hydrostatic pressure on the activation energy of the diffusion constant.

This activation energy is the energy needed to separate the polymer chains in order to form a "hole" to accommodate the permeant. At high hydrostatic pressures the density of the polymer increases. This increases the cohesive forces between chain segments and also favors crystallization. As a consequence, it becomes more difficult for a diffusing molecule to separate chain segments and the activation energy increases. It can readily be seen from equation (8) that this increase in activation energy results in a decrease in the permeability constant.

All of the above discussion is strictly valid only if the permeant does not dissolve in the membrane to an appreciable extent. As long as the concentration of the permeant in the membrane is small, Henry's law, which requires that the solubility be proportional to the vapor pressure, and Fick's law, which requires that the diffusion rate be proportional to the concentration gradient, are obeyed. As a result, equations (3) and (7) are meaningful in the sense that P , D , and S are constants independent of the ingoing pressure and the discussion given in the previous paragraphs is valid.

On the other hand, if the permeant is very soluble and swells the membrane appreciably, then the activity ceases to be proportional to the concentration. Henry's law is no longer obeyed, and the solubility coefficient, S , ceases to be a constant. In addition, the plasticization of the membrane reduces the activation energy, E_D , and as a result the diffusion constant, D , increases and Fick's law is no longer obeyed. As a result of both of these effects the permeability constant, P , ceases to be a constant, and becomes a variable dependent on the ingoing pressure, P_1 , the past history of the membrane, and the state of aggregation of the permeant. Such situations, exemplified by the permeation of water through nylon are very complex. Details can be found elsewhere (1, 2, 3, 4, 18) and will not be reviewed here. Under such circumstances a simple mathematical analysis becomes impossible and it is difficult to make reliable predictions from theory alone as to what effect, if any, the hydrostatic pressure has on such systems. It becomes more easy to determine this experimentally and the data in Table 1 show that the hydrostatic pressure had the same influence on the permeation of water through nylon as it had on the permeation of water through polyethylene. This suggests that the complexity of such situations does not alter the validity of the conclusion that hydrostatic pressure does not increase the permeability.

The reasons why the hydrostatic pressure has so little effect on the permeability can be summarized in loose terms as follows: The hydrostatic pressure favors any process in which the volume decreases. The permeation process might involve a small volume decrease or a small volume increase.

If both sides of the membrane are pressurized then no permanent change in the volume of the total pressurized liquid occurs. If only one side is pressurized then a permanent reduction in the volume of the pressurized side occurs when the permeant leaves this side. However, this volume reduction is small in the sense that the energy change accompanied by it, which is

equal to the pressure-volume product, is small in comparison with the activation energy. For instance, the energy needed to transfer one mole of water to a pressure of 1000 atmospheres is 18 liter-atmospheres or 0.43 kcal. This is small compared to the usual activation energies which are about 10 kcal. (19).

In addition to the above permanent change in volume, a transient change in volume might occur when the permeating molecule is in the "activated" state in which it is in the process of migration from one "hole" to another. This process disrupts the order and crystallinity of the polymeric network and this loss of order can be expected to result in a volume increase.

Since both of these volume changes are small, the hydrostatic pressure has no overwhelming effect on the permeation. Whether the small effect which the hydrostatic pressure does have is a decrease or an increase in permeation depends on the relative magnitude of these volume changes.

EXPERIMENTAL DETAILS

Permeability Measurements at Low Water Vapor Pressure. The apparatus and procedure used were similar to those of Doti, Aiken and Mark (20). Thin membranes of butyl rubber or polyurethane were subjected to vapor pressures of 5.8 and 17.5 mm on the ingoing side and the pressure increase in the evacuated receiving section (the volume of which was about 6 liters) was followed for 1-2 weeks for butyl rubber and for 24 hours for polyurethane. The permeability was determined from the slopes of the steady-state permeation rates.

The membranes used for these measurements were prepared by grinding cured sheets to thicknesses of about 20 mils. The butyl rubber was compounded and cured at our Laboratory and was found to have a permeability constant of 12×10^{-10} gram water/cm²/cm/hr/mm Hg. The polyurethane, which was the polyether based polyurethane PR-1538 manufactured by the Product Research Company, was supplied in cured form by the manufacturer and was found to have a permeability of 30×10^{-8} gram water/cm²/cm/hr/mm Hg. Later, results of measurements carried out by Herrick (8) at 3000 psi became available. His permeability constant, 6×10^{-8} gram water/cm²/cm/hr/mm Hg, differed from ours and it was at first suspected that the different origins of the specimens were responsible. In order to rule this out, a specimen cut from the 12-mil thick sheet, which had been cast by Herrick for his experiments, was obtained and tested at low vapor pressure. The permeability found, 37×10^{-8} gram water/cm²/cm/hr/mm Hg, is in agreement with our previous result, and different from the results obtained at high hydrostatic pressure.

Permeability Measurements at High Hydrostatic Pressures were carried out using pouches made from butyl rubber sheet which had previously been ground to a thickness of 20 mils. The pouches were made by the following method:

1. A piece of aluminum foil, 35 mm square, was centered on a 5 cm square of the butyl rubber.

2. A sheet of polyethylene was laid over the rubber-aluminum foil combination and laminated by heating in a press at approximately 120°C.

3. After cooling, the aluminum foil and the polyethylene adhering to it were cut out, leaving a center square of clean rubber.

4. An oblong 35 mm wide strip was cut from heavy duty aluminum foil, and a 35 mm long end portion thereof was covered on both sides with filter paper. This was placed on the rubber polyethylene laminate, with the filter-paper-covered section positioned on the center section of clean rubber and the bare aluminum foil section extending beyond one edge of the square.

5. A second butyl-polyethylene laminate square prepared as in steps 1-3 was placed on top of the first butyl-polyethylene laminate square and the filter-paper-covered aluminum strip, and heat sealed.

6. Removal of the aluminum-foil strip produced a filter-paper-lined pouch. This was filled with desiccant and heat sealed on the fourth edge.

These pouches were immersed in distilled water at atmospheric pressure and a constant temperature of 20°C. After several months, seven of these pouches were removed to a pressure vessel immersed in a constant temperature bath at 20°C, and exposed to distilled water at 10,000 psi hydrostatic pressure. Ten of these pouches were left as controls at atmospheric pressure.

After an 82 day immersion period, the pouches were weighed. The weight increase for those exposed at atmospheric pressure ranged between 0.028g and 0.035g. The permeability constant, 22×10^{-10} gram water/cm²/cm/hr/mm Hg, was calculated by multiplying the average of the weight increase (0.032g) by the wall thickness of the pouch, 20 mils (0.05 cm), and dividing the resulting product by the product of the area (25 cm²), the exposure time, 82 days (1968 hrs), and the water vapor differential (15 mm Hg). The latter is the difference between the vapor pressure of pure water (17.5 mm Hg) and that of saturated lithium chloride solution (2.6 mm Hg).

The weight increase of the pouches exposed to 10,000 psi pressure ranged between 0.008g and 0.010g. The permeability constant, 3.6×10^{-10} gram water/cm²/cm/hr/mm Hg, was calculated by multiplying the average weight increase, 0.009g, by the wall thickness, and dividing the resulting product by the product of the area, the exposure time, and the water vapor pressure differential, which in this case was 25 mm Hg. This value was calculated from equation (4) by substituting the vapor pressure differential for atmospheric conditions (15 mm Hg) for " p_0 , vap".

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